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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

α-Phenylphosphonatotrimethyltin(IV), $C_9H_{15}O_3PSn$, forms colorless crystals, mp=201° decomp., in the tetragonal space group $I4_1/acd$ with a=b=15.310(6), c=42.620(50) Å, V=9989.96 Å^3, Z=32 and ρ_{calc}=1.71 g cm^{-3}. The structure was solved by the heavy atom method to an R value of 0.046 for the 2578 reflections collected at 138±2K on an Enraf-Nonius CAD/4 automatic diffractometer using MoK$_\alpha$ radiation. The molecular units associate to form an infinite, one-dimensional polymer in which planar trimethyltin(IV) groups are axially-bridged by -O-P-O- linkages of the phenylphosphonate ligand to yield an →

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4.

$$\{[(CH_3)_3Sn]^+ [C_6H_5\overset{\overset{O}{\|}}{\underset{OH}{P}}-O-Sn(CH_3)_3-O-\overset{\overset{O}{\|}}{\underset{OH}{P}}-C_6H_5]^-\}_n \quad \text{Polymer.}$$
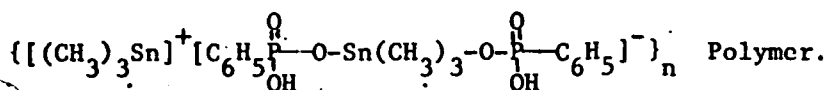
DEG.

20. almost perfect trigonal bipyramid at tin. The chains are linear at the tin atoms, but bent through a bite angle of $115.4(3)°$ at phosphorus. The chains propogate helically through the crystal, and each phenylphosphonate P=O and P-OH group is hydrogen bonded, holding adjacent helicies, turning in opposite directions, into two-dimensional sheets. The phenyl groups point outward from the center of the propogating helicies, separating the sheets from one another. Tin atoms occupy two non-equivalent environments, alternating metal atoms forming either two short or two long bonds to oxygen.

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$$\{[(CH_3)_3Sn]^+ [C_6H_5\overset{O}{P}-O-Sn(CH_3)_3-O-\overset{O}{P}-C_6H_5]^-\}_n \quad \text{Polymer.}$$

Oxy- and Thio Phosphorus Acid Derivatives of Tin.

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α-Phenylphosphonatotrimethyltin(IV) at 138 K.

A Unique, One-dimensional, Helical

$$\{[(CH_3)_3Sn]^+ [C_6H_5\overset{O}{\underset{OH}{P}}\!\!-\!\!O\!-\!Sn(CH_3)_3\!-\!O\!-\!\overset{O}{\underset{OH}{P}}\!\!-\!\!C_6H_5]^-\}_n$$
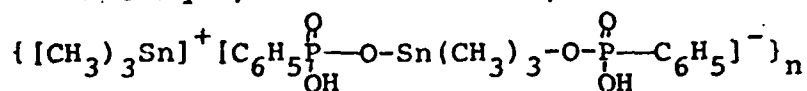
Polymer[1]

by

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We have been investigating the structures of organotin derivatives of thio phosphorus acids[1-3] which combine biocidal activity[4] in both halves of the molecule. The biocidal activity of the organotin moiety is now well-established, and such species have found extensive commercial application in the fields of fungicides, insecticides, bacteriocides and the protection of surfaces (ship hulls, pier pilings, etc.) from attack by marine organisms.[4] Particuarly attractive is the idea of combining the organotin species with ligands which are themselves biocidally active with the potential for enhanced activity in the compounds thus formed. The importance of phosphorus acids in _in vivo_ systems has thus led us to investigate the structures of organotin derivatives of ligands deriving from thio- or oxy-phosphorus acids.[1-3]

The possible structures this system can adopt are depicted in $\underline{A}$ to $\underline{E}$. The simplest is a monomeric structure containing a monodentate ligand and a four-coordinated tin atom as we have found in the solid ($\underline{O},\underline{O}'$-diethyl dithiophosphato)triphenyltin(IV),
$(C_6H_5)_3SnS\overset{S}{\overset{\|}{P}}(OC_2H_5)_2$,[2] shown in $\underline{A}$, but this configuration is virtually unique among the metal derivatives of such ligands.[5] Much more common is the chelated, five-coordinated monomer structure which can exist with anisobidentate or symmetrical chelation as shown in $\underline{B}$ and $\underline{C}$, respectively. We have found severely anisobidentate chelation in the dimeric tin(II) derivative bis($\underline{O},\underline{O}'$-diphenyl dithiophosphato)tin(II), $\{Sn[S\overset{S}{\overset{\|}{P}}(OC_6H_5)_2]_2\}_2$,[6] as well as in the octahedral diorganotin(IV) derivative, bis(dimethyl dithiophosphinato) dimethyltin(IV), $(CH_3)_2Sn[S\overset{S}{\overset{\|}{P}}(CH_3)_2]_2$.[1] Bis($\underline{O},\underline{O}'$-diisopropyl dithiophosphato)diphenyltin(IV), $(C_6H_5)_2Sn[S\overset{S}{\overset{\|}{P}}(OC_3H_7-i)_2]_2$, on the other hand, forms a tightly packed, centrosymmetric structure containing _trans-_

diorganotin(IV) units octahedrally coordinated by symmetrically chelating dithiophosphate ester ligands.[3] In these two latter diorganotin examples we have noted that the tin atoms lie along a unit cell axis at a distance that could be easily spanned by a bridging dithiophosphate ester group to give a polymer. We have termed this situation a "virtual polymer"[1,3] whose synthesis must await the development of suitable methods to convert the assemblage of monomers actually found into the isomeric polymer yet unrealized.[7]

When oxygen replaces sulfur in the phosphorus acids, bridging begins to predominate over chelation, and oligomeric and polymeric structures are found, as in D, which allow the more favorable axially-most-electronegative trigonal bipyramidal structures to form. The more electronegative oxygen would tend to prefer axial-sites where the p-character of the orbital it draws from the tin atom is maximized. In addition, the chelate ring forms (B or C) become sterically less favorable because of the smaller M-O interatomic distance and the increased difficulty of valence angle distortion.

The dimeric $[Cl_3SnPO_2Cl_2 \cdot POCl_3]_2$ is such an example in which eight-membered centrosymmetric rings are formed by dichlorophosphate groups doubly bridging two $Cl_3Sn \leftarrow O = PCl_3$ units to form an octahedral geometry at tin.[8] In the divalent tin series the tin(II) atoms in the hydrogen phosphate $(SnHPO_4)$,[9-11] bis(dihydrogen phosphate) $[Sn(H_2PO_4)_2]$,[12] phosphite $(SnHPO_3)$,[11] $Sn_2(OH)PO_4$,[11,13] $Sn_3(PO_4)_2$,[11,14] $Sn_3(O)(OH)PO_3$,[11,15] the two halophosphites $Sn_3PO_4F_3$,[11,16] and $SnFPO_3$[11,17] and $ClSnH_2PO_2$[18] are all bridged by three-atom, -O-P-O- linkages. In addition, in the transition metal series, the zinc(II) dialkyl

phosphinates are polymers containing alternating single and triple
-O-P-O- bridges[19-21] as are the zinc(II) and cobalt(II) diaryl
monothiophosphinates.[22] Molybdenum atoms are similarly bridged
by ethyl ammonium phosphonate groups in substituted heteropolyanions[23]
as are zinc(II) atoms by aminomethylphosphonate groups.[24] Berylium
atoms are alternately singly and triply bridged in the phosphinate
polymers, $[Be(R_2PO_2)_2]_2$.[25] Finally, tris[(dimethyltin(IV)] bis
(orthophosphate) octahydrate, $[(CH_3)_2Sn]_3(PO_4)_2 \cdot 8H_2O$, consists
of infinite ribbons in which octahedral, trans-dimethyltin(IV),
cis-diaquo groups are cis-linked by PO_4 tetrahedra to give eight-
membered rings in chair conformations.[26]

At least in principle, an ionic form as shown in E is also
possible. This latter possibility deserves mention since the onset
of ionic character would in this associated system be detectable
by the presence of long tin-ligand distances. Our 1978 review
of the structural tin literature[27] or its update[28] fail to
reveal a demonstrated example of such a situation which would have
important implications for certain solid state physical properties
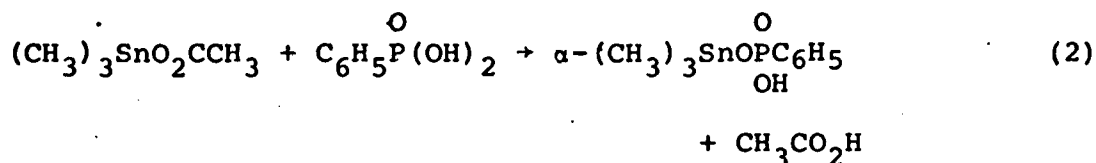such as electrical conductivity.

The title compound was prepared as in Eq. 1 by the action of
trimethyltin chloride on phenylphosphonic acid in water:[29]

$$(CH_3)_3SnCl + C_6H_5\overset{O}{P}(OH)_2 \rightarrow \alpha\text{-}(CH_3)_3SnO\overset{O}{\underset{OH}{P}}\text{---}C_6H_5 + HCl \qquad (1)$$
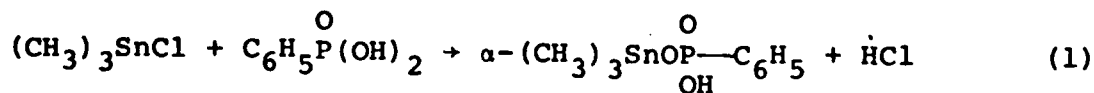
The same modification is obtained by refluxing trimethyltin acetate
with the acid in water:

|⁻J(Sn-C- H)| = 69 Hz in solution and exhibits a doublet

$$(CH_3)_3SnO_2CCH_3 + C_6H_5\overset{O}{\overset{\|}{P}}(OH)_2 \rightarrow \alpha\text{-}(CH_3)_3Sn\overset{O}{\underset{OH}{\overset{\|}{OPC_6H_5}}} \qquad (2)$$

$$+ CH_3CO_2H$$

Rapid precipitation of the α-form, however, yields a β-modification whose X-ray powder diffraction patterns show no trace of the α-form. The β-modification is also exclusively obtained by reaction of the monosodium salt of the acid with trimethyltin chloride in a minimum of water solvent.[29]

The colorless, crystalline α-product which can be crystallized from donor solvents such as methanol, acetone, THF or pyridine without inclusion of solvent in the crystals, decomposes at 201° to release methane and form $(CH_3)_2SnPO_3C_6H_5$, and yields a proton nmr $|^2H(^{119}Sn\text{-}C\text{-}^1H)| = 69$ Hz in solution. The doublet

tin-119m Mössbauer spectrum with Quadrupole Splitting (Q.S.) = 3.92 and Isomer Shift (I.S.) = 1.35 mm s^{-1}.[29] These data are consistent with five-coordinated tin in a conventional trigonal bipyramidal environment, but neither the Mössbauer information derived for tin, nor the infrared of the PO_3 system allow the four structural possibilities, B-E, discussed above, to be distinguished. The mass spectrum, however, contains ditin fragments at m/e = 471(17.9%) which can be assigned to the $[(CH_3)_5Sn_2PO_3C_6H_5]^+$ ion, and at 441(5.1%) which would correspond to the further loss of two methyl groups from the former species, suggesting a covalent oligomeric or polymeric situation (as in D) or an ionic array (as in E).

To test which of these possibilities exists, we have carried out a single crystal X-ray diffraction study on the title compound, the results of which we now report.

Experimental Section

Crystal Data. Colorless crystals of the title compound were obtained over a period of two weeks by cooling a methanol solution, and were stable to both atmospheric moisture[29] and X-rays. Crystal data are listed in Table I.

Details of our diffractometer, method of data collection and data reduction have been outlined previously.[2] Specific parameters pertaining to the collection of the data set are summarized in Table II. The structure factors for each reflection were assigned individual weights.[2]

Structure Determination and Refinement

The positions of the tin atoms were obtained by direct methods using MULTAN.[30]   It was found that the 32 tin atoms in the unit cell were comprised of 16 on each of two special positions: 1/4, $\underline{x}$, 1/8 (Wyckoff notation $\underline{e}$, space group $I4_1/acd$) and $0,0,\underline{z}$ ($\underline{d}$). This solution was confirmed by the successful use of these two positions to interpret the 28 most intense peaks in a three-dimensional Patterson map.[31]   Following two cycles of full matrix, isotropic, least-squares refinement, a difference Fourier yielded the positions of the remaining non-hydrogen atoms.   All atoms were refined aniso-tropically to a final R value of 0.046 (weighted R = 0.048).   Final shifts in both positional and thermal parameters were less than one-fifth of their corresponding estimated standard deviation.

A final difference Fourier map contained areas of residual electron density of intensity, $\underline{ca}$. 1e $Å^3$.   Although these peaks correspond to probable hydrogen atom locations, no systematic attempt was made to assign the latter.

Final atomic parameters (both positional and thermal) and intra-molecular distances and angles are listed in Tables III-VI, respectively. The asymmetric unit, with atomic labeling, is diagramed in Figure 1.

Description and Discussion of the Structure

In gross feature, α-phenylphosphonatotrimethyltin(IV) crystallizes in an infinite, one-dimensional, helical polymer as shown in Figure 1, in which planar trimethyltin(IV) units are axially-bridged by three-atom, -O-P-O- linkages from the phenylphosphonate ligand.

The geometry at each tin is almost perfectly trigonal bipyramidal [O(1)-Sn(1)-O(1') = 178.0(2)°; O(2)-Sn(2)-O(2') = 175.9(2)°]. Within each of the two distinct trimethyltin groups, one tin-carbon bond lies on a two-fold axis [Sn(1)-C(7) or Sn(2)-C(9)], establishing perfect planarity of the separate $[C_3Sn]$ moieties. This finding is in agreement with the infrared data from which it is possible to assign the tin-carbon $\nu_{asym}(SnC_3)$ stretching frequency at 532 cm^{-1}, but no lower frequency absorption band is available to assign to the $\nu_{sym}(SnC_3)$ mode. In the Raman spectrum, on the other hand, an intense absorption at 515 cm^{-1} can be assigned to this latter mode. Thus the trimethyltin(IV) group obeys the vibrational spectroscopic selection rules for the planarity confirmed in the structure.

Although the virtual linearity of the O-Sn-O bonds requires linearity of the polymer in the vicinity of the tin atoms, the chains are bent through the tetrahedrally coordinated phosphorus atoms of the phosphonate ligand at an -O(1)-P(1)-O(2)- angle of 115.3(3)°. The chains thus propogate through the crystal in a helical fashion, with adjacent helicies turning in opposite directions.

Hydrogen bonding interactions, which we assume are binding the P-OH and O=P groups in each ligand bring, together the first and fourth phosphonate ligands of one helix (shown schematically in Figure 2a), with the second and third phosphonate ligands of the second helix of opposite hand (Figure 2b). The second and third

ligand units of the first helix

also form hydrogen bonds to the first and fourth phosphonate ligand groups of another helix adjacent to it (Figure 2c) which is of the opposite hand. The stack of helicies held at regular intervals by hydrogen bonds creates infinite, two-dimensional sheets. An ORTEP representation of part of one sheet is shown in Figure 3. As can be seen in Figure 4, the phenyl groups point outward from the center of the propogating helicies, separating the independent sheets of helicies from one another.

Four pairs of helical chains, each pair consisting of two helicies of opposite hand, are found in the unit cell as seen in Figure 5. There are thus portions of four sheets propogating in the $\underline{ab}$-plane contained in each unit cell. Within any sheet two he cal chains are contained in the $\underline{b}$-dimension of the unit cell.

A more detailed description of the bonding within each chain requires the identification of the three different P-O bonds of each phosphonate group. We assume that the P=O and P-OH units bound together between adjacent chains by hydrogen bonding can be identified, despite our not having located the hydrogen atoms. Fortunately, structural data for the parent, phenylphosphonic acid, $C_6H_5\overset{O}{\overset{\|}{P}}(OH)_2$, which also forms a hydrogen-bonded solid are available. The P=O distance is, as expected, shortest at 1.496 Å, while the P-OH bond is at an average distance of 1.545 Å.[32] These distances change to 1.489 and 1.563 Å, respectively, in the singly-ionized sodium acetyl-phosphonate acetic acid solvate, $CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{P}}(OH)ONa$,[33] and to 1.500 and 1.569 Å, respectively, in the zwitterionic 2-aminoethylphosphonic acid (β-ciliatine).[34]

In the title compound two of the oxygen atoms [O(2) and O(3)] lie within a hydrogen bonding distance of the symmetry-related oxygen atoms [O(3) and O(2), respectively] of an adjacent polymer chain. The hydrogen bonds thus formed are relatively short[35] (2.589 Å), essentially the same as the mean distance found in the parent acid.[32] Since according to the scheme in structure F, one must be the P=O and the other the P-OH system, the identification can be based upon the respective phosphorus-oxygen interatomic distances which specify P(1)=O(2) at 1.516(5) Å as the double-bonded group and P(1)-O(3) at 1.580(6) Å as the P-OH group. The remaining oxygen bonded to phosphorus [O(1)-P(1) = 1.492(6) Å] is thus deprotonated and ester-bound to tin [O(1)-Sn(1) = 2.240(6) Å]. The marked shortening of the P(1)-O(1) ester bond relative to the parent acid P-OH system (1.545 Å) is also seen in the [PO$_2$Cl$_2$]$^-$ anion which doubly bridges octahedral tin(IV) units in the [Cl$_3$SnOPCl$_3$·PO$_2$Cl$_2$]$_2$ dimer,[8] but not in the [trans-(CH$_3$)$_2$Sn]$_3$(PO$_4$)$_2$·8H$_2$O where the double -O-P-O- bridges exhibit P-O ester distances in the range 1.52-1.56 Å.[26] The shortening of this P(1)-O(1) bond in the title compound possibly arises as a consequence of the molecular packing which is dictated by the formation of interchain hydrogen bonding. The relative lengthening of the P(1)=O(2) bond with respect to the parent acid, presumably arises because the O(2) atom engages in bifurcated coordination, forming both a dative bond to Sn(2) and a hydrogen bond to O(3). This has the effect of lengthening this bond so that its interatomic distance [1.516(5) Å] becomes roughly comparable to the P(1)-O(1) distance at 1.492(6) Å, which is different by only five standard deviations.

Confirmation for these assignments can come from a comparison of the respective distances these P-O units make with their tin bonding

partners, where the doubly-bonded phosphorus-oxygen linkage, assigned as P(1)=O(2), should be adjacent to a long, dative bond to tin [O(2)→Sn(2) = 2.319(5) Å]. Likewise, the P(1)-O(1) bond is found contiguous to a relatively shorter covalent bond to tin [O(1)-Sn(1) = 2.240(6) Å].

Reversing the assignments of the P(1)-O(1) and P(1)-O(2) systems to the P=O and P-O ester linkages, respectively, satisfies the criterion that the P=O bond be the shortest connection to phosphorus made by the oxygen atom, but that requires the hydrogen bonds to be established as in the less likely scheme G. In addition, the expectation that the P=O bond should make a longer, dative O→Sn bond to tin and that the O-Sn ester bond should be shorter are disappointed. For these reasons we prefer the first assignment (F) described above.

Comparison of the tin-oxygen bond distance contiguous to the P=O group [Sn(2)-O(2) = 2.319(5) Å] can be drawn with the dative O→Sn interatomic distance of 2.29 Å in nitratotriphenyl(triphenyl-phosphine oxide)tin(IV) which also involves a trigonal bipyramidal triorganotin(IV) center, axially-coordinated by oxygen.[36] A somewhat shorter connection is found in the octahedral anion, $[Cl_5Sn{\leftarrow}O{=}PCl_3]^-$, where the dative O→Sn interatomic distance is 2.27 Å,[37] and in the cis-octahedral complex $SnCl_4{\cdot}2O{=}PCl_3$ where the mean Sn-O distance is 2.28 Å.[38]

Comparison of the ester tin-oxygen bond distance [Sn-O(1) = 2.240(6) Å] with those in the $[Cl_3SnOPCl_3{\cdot}PO_2Cl_2]_2$ dimer where the bridge PO_2Cl_2 groups exhibit distances of 2.119 and 2.120 Å to the octahedral tin atoms,[8] and with those in $[(CH_3)_2Sn]_3(PO_4){\cdot}8H_2O]$ in which there are three tin environments.[26] In the latter structure two aquated tin atoms whose geometries lie between tetrahedral and

octahedral establish ester bridge bonds of 2.02 and 2.04 Å, while

a $\underline{trans}$-$(CH_3)_2Sn$ unit of octahedral structure makes ester bridge

bonds of 2.17 and 2.18 Å.[26] The Sn-O ester bond in the title compound

is thus longer than the corresponding bonds discussed above, and is

considerably longer than the single bond value of 2.10 Å.[26,35]

Because the two tin-oxygen distances at each tin center are

symmetry related [by the two-fold axes along Sn(1)-C(7) and Sn(2)-

C(9)], and must, therefore, be equal, the conventional bridging

arrangement, as in $\underline{D}$, must be ruled out. Instead, we have in the

title compound a situation in which there are two non-equivalent

tin sites, with alternate tin atoms making two short [Sn(1)-O(1) =

Sn(1)-O(1') = 2.240(6) Å] or two long [Sn(2)-O(2) = Sn(2)-O(2') =

2.319(5) Å] bonds to oxygen. An O(1)-Sn(1)-O(1') angle of 178.0(2)°

is associated with the short Sn-O bonds, and an O(2)-Sn(2)-O(2')

angle of 175.9(2)° is associated with the long Sn-O bonds. This is

the only example of which we are aware of an associated organotin

polymer in which the chains consist of alternating tin environments.[27-8,3]

This arrangement is probably best described in terms of structure $\underline{H}$

as a combination of trimethyltin(IV) cations and bis-(phenylphosphonato)

trimethyltin(IV) anions, $[C_6H_5\overset{O}{\underset{OH}{P}}-OSn(CH_3)_3O\overset{O}{\underset{OH}{P}}-C_6H_5]^-$, alternating

in a helical array. The tin atoms are not sufficiently different

to be distinguished by ^{119m}Sn Mössbauer spectroscopy, but this is

not surprising since even the tin atoms in the five- and six-coordinated

double salt $[(CH_3)_3Sn\cdot terpy]^+[(CH_3)_2SnCl_3]^-$ are barely distinguishable

by Mössbauer spectroscopy.[42]

The phosphorus atoms, of which there is only one kind, are found

at the center of a distorted tetrahedron with three oxygen atoms and

a phenyl group as nearest neighbors. Contrary to the expectations

of isovalent hybridization, the three O-P-C angles involving carbon

are as an average (108.1°) smaller than the average of the three angles

-O-P-O (110.7°). However, this value of the mean is mainly a result of the

opening of the O(1)-P-O(2) angle which involves the oxygen atoms

connected to tin to 115.3(3)°. The comparable bite angle of the

double -O-P-O- bridges between the octahedral tin(IV) atoms of

di(phosphoryl trichloride) hexachloroditin(IV), $[(Cl_3SnOPCl_3)^+$

$(PO_2Cl_2)^-]_2$, is 118.0°,[8] and a mean value of 111.4° is found in

tris[dimethyltin(IV)bis(orthophosphate) octahydrate, $[(CH_3)_2Sn]_3$

$(PO_4)_2 \cdot 8H_2O$.[26] The comparable mean value for the singly-bridged

portion of the bis(diorganophosphinato)zinc(II) polymer is 116.8°.[21]

Table I. Crystal Data

formula	$C_9H_{15}O_3PSn$
fw	320.90
crystal class	tetragonal
spage group[a]	$I4_1/acd$
a,b[b]	15.310(6) Å
c[b]	42.620(59) Å
V	9989.96 Å^3
Z	32
F(000)	5056
μMoK$_\alpha$	21.7 cm^{-1}
data crystal dimensions	0.17x0.15x0.17 mm

[a]From systematic absences: hkl, h+k+l = 2n+1; hk0, h = 2n+1; 0kl, l = 2n+1; hhl, 2h+l ≠ 4n.

[b]Based upon ±2θ values of 64 reflections, and using MoK$_\alpha$ radiation (λ = 0.70926 Å).

Table III. Final Position ($\times 10^4$) Parameters for α-$(CH_3)_3SnO\overset{O}{\overset{\|}{P}}(OH)C_6H_5$[a]

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$
Sn(1)	5000(0)	0(0)	637.2(2)
Sn(2)	2500(0)	2156.9(5)	1250(0)
P(1)	4415(1)	2143(2)	792.9(4)
O(1)	4310(4)	1290(4)	628(1)
O(2)	3961(3)	2211(4)	1108(1)
O(3)	5416(4)	2334(5)	85.(1)
C(1)	4033(6)	2993(5)	538(2)
C(2)	3546(6)	2769(6)	273(2)
C(3)	3236(7)	3434(6)	73(2)
C(4)	3426(7)	4298(6)	135(2)
C(5)	3925(7)	4529(6)	394(2)
C(6)	4214(6)	3864(6)	604(2)
C(7)	5000(0)	0(0)	1123(3)
C(8)	3883(7)	-527(7)	410(3)
C(9)	2500(0)	3560(9)	1250(0)
C(10)	2139(6)	1402(7)	853(2)

[a]Estimated standard deviations in parentheses.

Table II. Data Collection Parameters for α-$(CH_3)_3SnOP(O)(OH)C_6H_5$

Diffractometer	Enraf-Nonius CAD/4
Radiation	MoK$_{\alpha}$ (0.7121 Å)
Temperature	138±2 K
Scan Technique	θ-2θ
Limit	$\theta \leq 2\theta \leq 53°$
Scan Time	40s
Scan Angle	(0.7+0.20 tanθ)
Aperature Width	(2.5+0.86 tanθ)
Aperature Height	6 mm
Aperature Distance	173 mm
Monitor Reflection	$\bar{4}$ 0 8
Intensity Monitor	2500s
Max. Fluctuation in Monitor	<1.2%
Orientation Monitors	200 reflections
Number of Unique Data	2578
Number of Observed Data[a]	2296
Corrections	Lorentz
	Polarization
	Absorption
	Anomolous Dispersion

[a]$I > 2\sigma(I)$

Table IV. Final Anisotropic $(\times 10^4)$ Thermal Parameters for $\alpha\text{-}(CH_3)_3SnO\overset{O}{P}(OH)C_6H_5$ [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	192(4)	289(4)	179(4)	0(0)	0(0)	45(3)
Sn(2)	142(4)	260(4)	173(4)	0(0)	-11(3)	0(0)
P(1)	94(8)	377(11)	176(9)	-18(8)	-4(7)	-7(8)
O(1)	218(29)	281(31)	411(33)	-21(26)	-45(25)	106(24)
O(2)	93(24)	404(33)	184(25)	22(23)	5(20)	-9(22)
O(3)	155(29)	736(50)	248(28)	-44(30)	-28(23)	-85(29)
C(1)	321(43)	239(41)	189(35)	-7(30)	72(32)	-32(33)
C(2)	260(41)	302(43)	238(37)	5(32)	-6(32)	-57(34)
C(3)	414(53)	290(46)	339(47)	88(36)	-35(38)	-32(40)
C(4)	453(55)	327(48)	311(43)	43(38)	88(40)	3(41)
C(5)	430(55)	346(50)	319(43)	-59(38)	127(40)	3(41)
C(6)	439(51)	358(47)	130(33)	-49(32)	36(33)	-138(40)
C(7)	54(48)	737(99)	343(64)	0(0)	0(0)	59(56)
C(8)	392(57)	491(62)	535(59)	-185(50)	-200(48)	65(47)
C(9)	434(81)	294(72)	683(98)	0(0)	102(76)	0(0)
C(10)	291(46)	572(63)	288(42)	-206(43)	-19(36)	-78(44)

[a] Estimated standard deviations in parentheses

Table V. Final Interatomic Distances (Å) in α-$(CH_3)_3SnO\overset{O}{\overset{\|}{P}}(OH)C_6H_5$[a]

Sn(1)-O(1)	2.240(6)	P(1)-O(1)	1.492(6)
Sn(1)-O(1')	2.240(6)	P(1)-O(2)	1.516(5)
Sn(1)-C(7)	2.070(13)	P(1)-O(3)	1.580(6)
Sn(1)-C(8)	2.124(11)	P(1)-C(1)	1.793(9)
Sn(1)-C(8')	2.124(11)		
Sn(2)-O(2)	2.319(5)	C(1)-C(2)	1.396(12)
Sn(2)-O(2')	2.319(5)	C(2)-C(3)	1.410(13)
Sn(2)-C(9)	2.148(14)	C(3)-C(14)	1.380(13)
Sn(2)-C(10)	2.122(9)	C(4)-C(5)	1.388(13)
Sn(2)-C(10')	2.122(9)	C(5)-C(6)	1.426(13)
		C(6)-C(1)	1.391(12)

[a] Estimated standard deviations in parentheses.

Table VI. Final Interatomic Angles (deg.) in α-$(CH_3)_3SnO\overset{O}{P}(OH)C_6H_5$[a]

O(1)-Sn(1)-O(1')	178.0(2)	Sn(1)-O(1)-P(1)	135.5(3)
O(1)-Sn(1)-C(7)	91.0(2)	Sn(2)-O(2)-P(1)	132.2(3)
O(1)-Sn(1)-C(8)	87.0(3)		
O(1)-Sn(1)-C(8')	92.1(3)	O(1)-P(1)-O(2)	115.3(3)
O(1')-Sn(1)-C(7)	91.0(2)	O(1)-P(1)-O(3)	110.0(3)
O(1")-Sn(1)-C(8)	92.1(3)	O(1)-P(1)-C(1)	108.3(4)
O(1')-Sn(1)-C(8')	87.0(3)	O(2)-P(1)-O(3)	106.9(3)
C(7)-Sn(1)-C(8)	117.1(3)	O(2)-P(1)-C(1)	109.7(4)
C(7)-Sn(1)-C(8')	117.1(3)	O(3)-P(1)-C(1)	106.2(4)
C(8)-Sn(1)-C(8')	125.8(4)		
		P(1)-C(1)-C(2)	119.1(7)
O(2)-Sn(2)-O(2')	175.9(2)	P(1)-C(1)-C(6)	120.6(7)
O(2)-Sn(2)-C(9)	88.0(2)	C(2)-C(1)-C(6)	120.4(8)
O(2)-Sn(2)-C(10)	93.6(3)	C(1)-C(2)-C(3)	119.4(8)
O(2)-Sn(2)-C(10')	93.6(3)	C(2)-C(3)-C(4)	120.4(9)
O(2)-Sn(2)-C(10')	88.6(3)	C(3)-C(4)-C(5)	120.8(9)
O(2')-Sn(2)-C(9)	88.0(2)	C(4)-C(5)-C(6)	119.2(9)
O(2')-Sn(2)-C(10)	88.6(3)	C(5)-C(6)-C(1)	119.7(8)
O(2')-Sn(2)-C(10')	93.6(3)		
C(9)-Sn(2)-C(10)	123.0(3)		
C(9)-Sn(2)-C(10")	123.0(3)		
C(10)-Sn(2)-C(10')	114.0(4)		

[a] Estimated standard deviations in parentheses

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(39) A similar situation has been noted in two independent determinations[40,44] of the structure of $(CH_3)_3SnO_2SCH_3$ which consists of crystallographically independent tin sites bridged by sulfinate ligands in an alternating one-dimensional array. As with the title compound, each tin atom lies on a two-fold axis, and is bonded to two identical oxygen atoms, but these differ in the two sites. However, this difference between pairs of tin-oxygen bond distances was found to be only three standard deviations in one determination,[40] and zero in the other.[41]

It is (39). A similar situation has been noted in two determinations[40,4-] of the structure of $(CH_3)_3SnO_2SCH_3$ which consists of two independent

tin sites bridged by sulfinate ligands in an alternating, one-dimensional array. As in the title compound, each tin atom lies on a two-fold axis and is bonded to two identical oxygen atoms which differ in the two sites. However, this difference between pairs of tin-oxygen bond distances was found to be only three standard deviations in one study,[40] and zero in the other.[41] It is worth noting that these polymer chains also adopt a helical configuration, but the inability to form hydrogen bonds precludes the association of the helicies into sheets as in our structure.

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Figure Captions

Figure 1.   The asymmetric unit of α-phenylphosphonatotrimethyltin(IV),
showing the atom numbering scheme. Primed and doubly
primed atoms are related to unprimed atoms by the two-fold
axes   Sn(1)-C(7) and Sn(2)-C(9), respectively.

Figure 2.   Schematic representation of the hydrogen bonding between
adjacent helicies. Solid lines (   ) represent helices
propagating in a clockwise manner in the direction of the
associated arrow; numbered boxes indicate PO_3 units within
any given helix. Hydrogen bonded PO_3 groups are linked
by dotted lines (   ).

Figure 3.   ORTEP drawing of two adjacent helices, of opposite hand,
linked by hydrogen bonds (   ).

Figure 4.   A pair of adjacent helices, viewed along the axis of pro-
pagation. The upper (   ) and lower (   ) helices propagate
out of the page in an anti-clockwise and clockwise manner,
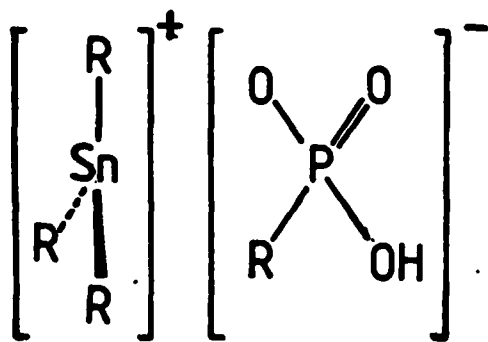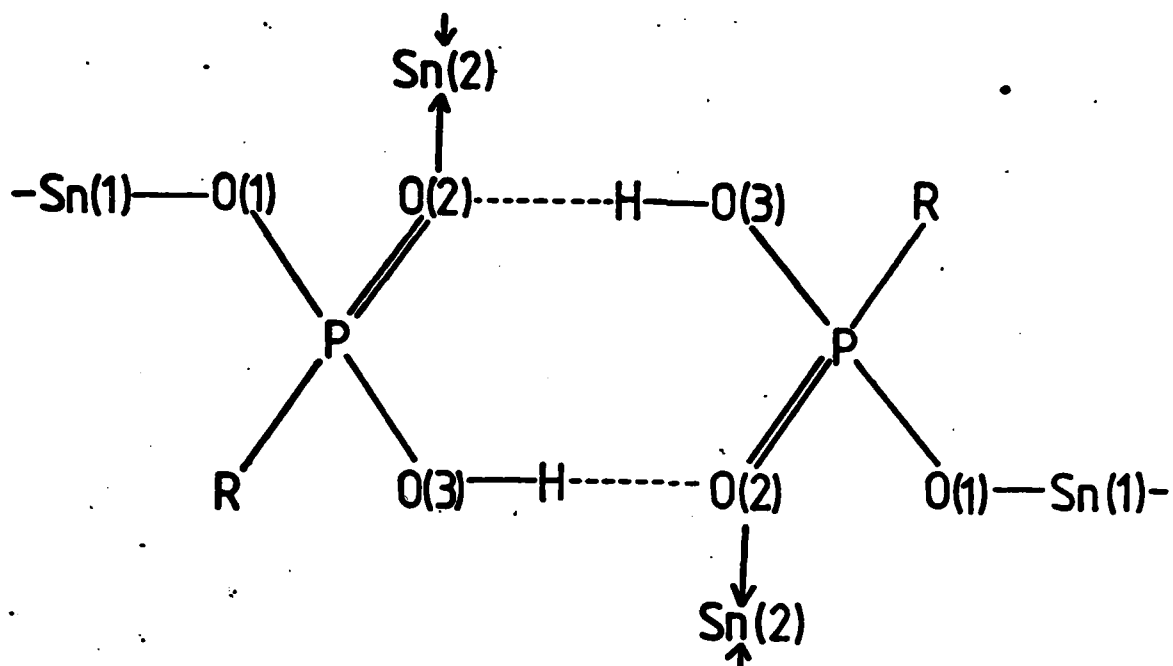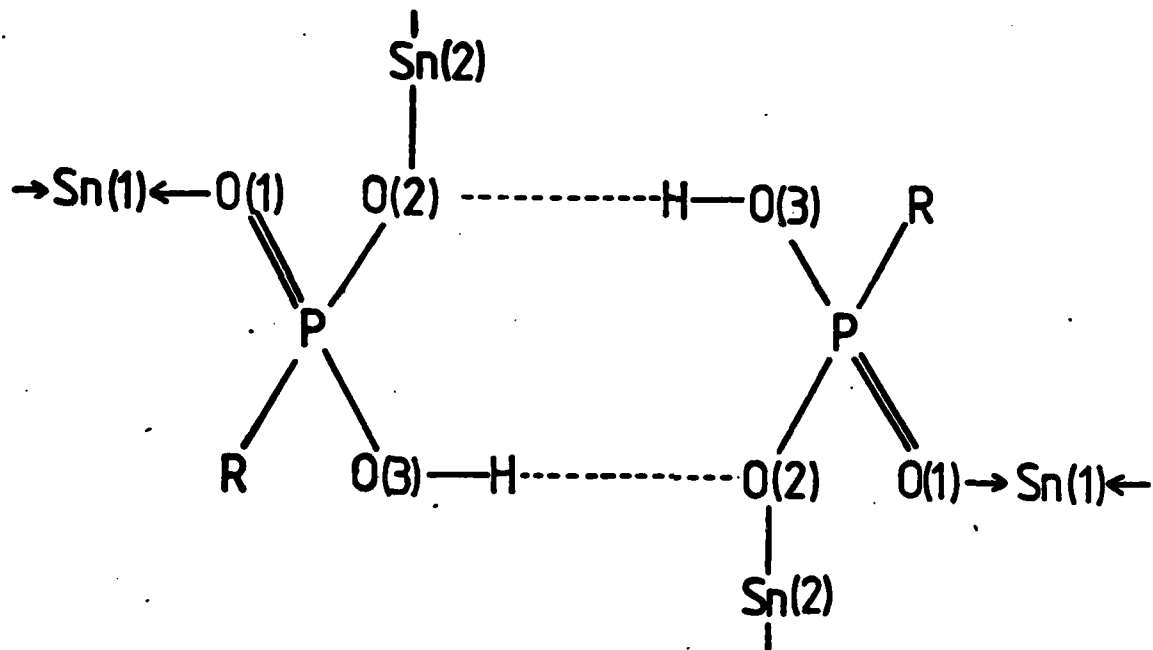respectively. Hydrogen bonds between helices are dotted.

A

B

C

D

E

F

G

$$\left[\begin{array}{c} R \\ \rightarrow Sn \leftarrow \\ R \quad R \end{array} \right]^{+} \left[\begin{array}{c} R \quad OH \\ \backslash P \diagup \\ \parallel \\ O - O - Sn - O - O \\ R \quad R \quad \parallel \\ R \quad P \\ HO \quad R \end{array} \right]^{-}$$
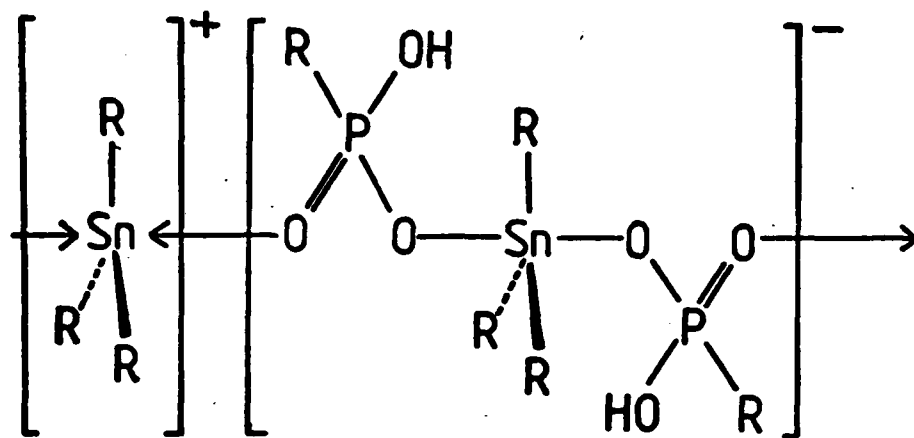
<u>H</u>

fig 1

Fig 2

Fig 3

Fig 4